

# *Open circuit voltage recovery of discharged and shorted nickel-cadmium cells*

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The open circuit voltage recovery transient of a positive-limited nickel-cadmium cell has been theoretically analysed taking into account the double-layer charging process, polarization due to charge transfer, mass transfer and ohmic resistance in the cell, and self-discharge due to any internal electronic short. Expressions have been obtained for charge transfer and mass transfer polarization. Experimental data on open circuit voltage recovery transients obtained for nickel-cadmium cells indicate that the rate of the electrode reaction at the positive electrode of the cells is controlled by mass transfer process.

## **Nomenclature**

$B$	integration constant in Equation 16 ( $B < 0$ )	$I_{\text{far}}$	current due to charge-transfer process (faradaic current) (A)
$B_1$	integration constant in Equation 22 ( $B_1 < 0$ )	$J_e$	current flowing through an internal short that may be present in the cell (A)
$C_c$	double layer capacitance of the cell cathode ( $\text{F m}^{-2}$ )	$J_i$	current flowing through the cell due to double layer charging as well as charge-transfer reactions at the electrodes as defined by Equation 2 (A)
$C$	capacity of the nickel-cadmium cells (A h)	$K_c$	constant, characteristic of diffusion for the charging reaction at the cell cathode (A)
$C_0^o$	concentration of the oxidized species in the porous bulk of the electrode (M)	$n_c$	number of electrons involved in the charging reaction at the cell cathode
$D_o$	diffusion coefficient of the oxidized species ( $\text{m}^2 \text{s}^{-1}$ )	$R_e$	the equivalent resistance of an internal short ( $\Omega$ )
$E_a$	electrode potential of the cell anode (V)	$R_i$	internal (ohmic) resistance of the cell ( $\Omega$ )
$E_a^r$	reversible electrode potential of the cell anode (V)	$t$	time elapsed after the start of the experiment (s)
$E_c$	electrode potential of the cell cathode (V)	$V$	cell voltage at any instant during the open circuit voltage recovery process (V)
$E_c^r$	reversible electrode potential of the cell cathode (V)	$V^r$	reversible cell voltage defined as ( $E_c^r - E_a^r$ ) (V)
$f$	$F/RT$ where $F$ is Faraday constant, $R$ the universal gas constant and $T$ the absolute temperature ( $\text{V}^{-1}$ )	$\eta$	overpotential defined as ( $E - E^r$ ) (V)
$I_a$	net current at the cell anode (A)	$\eta_c$	overpotential at the cell cathode during open circuit voltage recovery defined as ( $E_c - E_c^r$ ) (V)
$I_c$	net current at the cell cathode (A)		
$I_{o,c}$	exchange current of the reaction at the cell cathode (A)		
$\bar{I}_d$	limiting current for the forward reaction (A)		
$\bar{I}_d$	limiting current for the backward reaction (A)		

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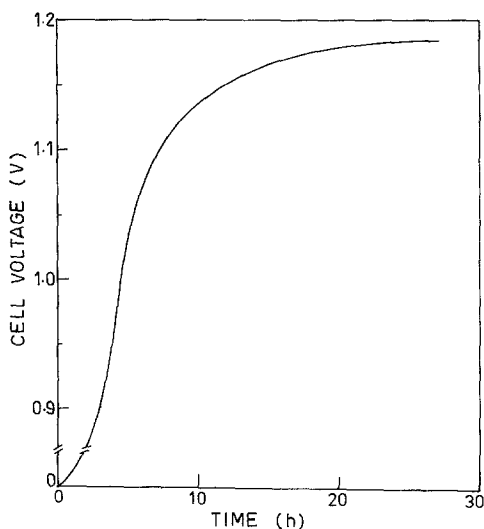


Fig. 1. Schematic illustration of a spontaneous open circuit voltage recovery transient of a nickel-cadmium cell from a discharged state.

## 1. Introduction

It is well established that when a nickel-cadmium battery cell is left on open circuit following a full discharge to zero volts, the cell voltage slowly increases with time and may eventually attain a value in the range of 1.0 to 1.2 V [1].

A schematic course of such a spontaneous recovery of the open circuit voltage of a nickel-cadmium cell from a discharged state is shown in Fig. 1. This feature of nickel-cadmium cells has found a practical application as a screening test for cells with and without a significant internal short [2].

A quantitative theoretical analysis of the cell voltage response to the open circuit stand period has been, however, lacking in the literature and is therefore developed here. Further, applicability of the analysis to predict certain failure modes has also been examined. Finally, a comparison of the theory with experiment has been carried out.

The spontaneous build-up of cell voltage on open circuit from an initial value of zero volts is equivalent to a spontaneous charging of the cell. The cell voltage is governed at any instant during this voltage recovery process by the relative concentrations of the oxidized and reduced species of the active material at the surface of the electrodes. Formally, the open circuit voltage recovery may thus be regarded as a succession of quasi-equilibrium states with a progressive increase in the open circuit voltage, caused by a slow diffusion of undischarged active materials from the deep interior of the porous electrodes towards the surface of the electrodes as shown schematically in Fig. 2. The resulting changes in the electrode potential lead to a double-layer charging process and a balancing faradaic process at each electrode. A quantitative formulation of the problem may be carried out with reference to a schematic view of the cell under test, shown in Fig. 3.

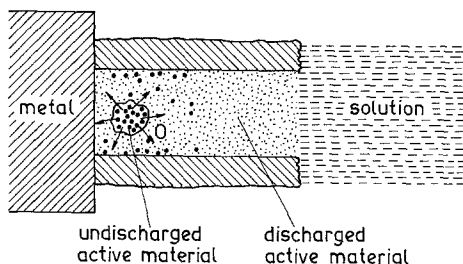


Fig. 2. Schematic representation of diffusion of undischarged active material from the interior of a pore to the surface.

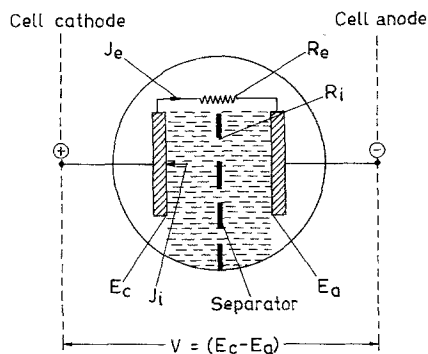


Fig. 3. Schematic representation of a nickel-cadmium cell on open circuit. An internal 'soft' short characterized by resistance,  $R_e$ , may be present due to cell degradation factors and which may cause self-discharge. Symbols defined in the Nomenclature.

The basic equations which govern the spontaneous charging process of the nickel-cadmium cell may be written with due regard to the facts that there is no external charging circuit in the present case, the voltage build-up is due to a self-charging process, and the internal cell current (if any) is due to a self-discharge process through any internal short that may be present. Accordingly, with reference to Fig. 3 it follows that

$$J_e - J_i = 0 \quad (1)$$

$$J_i = I_c = -I_a \quad (2)$$

$$J_e R_e = V \quad (3)$$

$$V = E_c - E_a - J_i R_i \quad (4)$$

$$I_c = -C_c \frac{dE_c}{dt} + I_{far,c} \quad (5)$$

$$I_a = -C_a \frac{dE_a}{dt} + I_{far,a} \quad (6)$$

It may be shown from the above that

$$\eta_c = E_c - E_c^r = \left( \frac{R_e + R_i}{R_e} \right) V - (E_c^r - E_a) \quad (7)$$

$$J_i = I_c = \frac{1}{(R_e + R_i)} (\eta_c + E_c^r - E_a) \quad (8)$$

The evaluation of  $I_{far,c}$  and  $I_{far,a}$  in Equations 5 and 6 requires a careful consideration of the processes involved.

When the rate of change of cell voltage or, equivalently, the rate of change of potential of the cell cathode is small, i.e. after a sufficiently long period of open circuit stand, the electrode potential may be regarded as near enough to the respective equilibrium potential so that the Butler-Volmer equation may be linearized to the following well-known form

$$I_{far} \left( \frac{1}{I_0} + \frac{1}{\bar{I}_d} - \frac{1}{\bar{I}_d} \right) = -nf\eta \quad (9)$$

where  $\eta = E - E^r$ . The reversible potential,  $E^r$ , though not accessible for direct measurement, does exist. Its value is appropriate to the surface concentrations of the electroactive species at the moment when the electrode potential reaches the beginning of the polarization range considered.

In the present case the term  $1/\bar{I}_d$  in Equation 9 can be neglected in comparison with the other two

terms since  $\tilde{I}_d$  is a large quantity (compared to  $\bar{I}_d$ ) for a completely discharged cell. On the other hand, diffusion of a charged form of electroactive species tends to occur from a 'limited source' to a 'limited sink' as shown schematically in Fig. 2. The term  $1/\tilde{I}_d$  is therefore important, and thus

$$I_{\text{far}} \left( \frac{1}{I_o} + \frac{1}{\tilde{I}_d} \right) = -nf\eta \quad (10)$$

The value of  $\tilde{I}_d$  is governed by the thickness of the diffusion layer in the non-steady state which may be generally considered [3] to be given by  $(KD_o t)^{\frac{1}{2}}$  where  $K$  is a numerical constant. Hence,

$$\tilde{I}_d \approx nFAC_o^o \left( \frac{D_o}{Kt} \right)^{\frac{1}{2}} = \frac{K_c}{(t)^{\frac{1}{2}}} \quad (11)$$

Substituting for the value of  $\tilde{I}_d$  from Equation 11 into Equation 10 one obtains

$$I_{\text{far,c}} = -n_c f \eta_c \left[ \frac{1}{I_{o,c}} + \frac{(t)^{\frac{1}{2}}}{K_c} \right]^{-1} \quad (12)$$

Hence, using Equations 8 and 12, Equation 5 may be written as

$$J_i = I_c = -C_c \frac{dE_c}{dt} - (n_c f \eta_c) \left[ \frac{1}{I_{o,c}} + \frac{(t)^{\frac{1}{2}}}{K_c} \right]^{-1} = [\eta_c + (E_c^r - E_a)] \frac{1}{R_e + R_i} \quad (13)$$

or, since  $dE_c/dt = d\eta_c/dt$ ,

$$C_c \frac{d\eta_c}{dt} + n_c f \eta_c \left[ \frac{1}{I_{o,c}} + \frac{(t)^{\frac{1}{2}}}{K_c} \right]^{-1} + \frac{\eta_c}{(R_e + R_i)} + \frac{E_c^r - E_a}{(R_e + R_i)} = 0 \quad (14)$$

Equation 14 is a general expression for the open circuit voltage recovery of a positive-limited nickel-cadmium cell, taking into account double-layer charging and polarization due to charge transfer, mass transfer and ohmic resistance of the cell, in addition to any self-discharge through an internal electronic short that may be present.

A comparison of Equation 14 with experimental results may be carried out as follows by considering certain special cases.

### 1.1. When the mass transfer to the electrode is slow

When the mass transfer step is slow compared to the charge transfer step the corresponding situation is  $1/I_{o,c} \ll (t)^{\frac{1}{2}}/K_c$  in Equation 14. Therefore,

$$\frac{d\eta_c}{dt} + \left[ \frac{n_c f K_c}{C_c (t)^{\frac{1}{2}}} + \frac{1}{C_c (R_e + R_i)} \right] \eta_c + \frac{E_c^r - E_a}{C_c (R_e + R_i)} = 0 \quad (15)$$

Equation 15 is a linear, first-order differential equation whose solution is obtained by ignoring small-order terms in  $t^{-2}$ ,  $t^{-4}$  etc., as

$$\eta_c = -(E_c^r - E_a) \left[ \frac{(t)^{\frac{1}{2}}}{n_c f K_c (R_e + R_i) + (t)^{\frac{1}{2}}} \right] + B \exp \left\{ - \left[ \frac{t}{(R_e + R_i) C_c} + \frac{2n_c f K_c (t)^{\frac{1}{2}}}{C_c} \right] \right\} \quad (16)$$

Substituting Equation 16 into Equation 7 and rearranging, gives

$$V = \frac{(E_c^r - E_a) R_e}{R_e + R_i} \left[ \frac{n_c f K_c (R_e + R_i)}{n_c f K_c (R_e + R_i) + (t)^{\frac{1}{2}}} \right] + \frac{B R_e}{R_e + R_i} \exp \left\{ - \left[ \frac{t}{C_c (R_e + R_i)} + \frac{2n_c f K_c (t)^{\frac{1}{2}}}{C_c} \right] \right\} \quad (17)$$

Equation 17 is a general solution for the dependence of open circuit voltage,  $V$  (within a few mV from the final or equilibrium voltage), on time,  $t$ , at large times during the open circuit voltage recovery of a nickel-cadmium cell from a discharged state when mass transfer to the electrode is rate-controlling.

Consider the case of a cell which has no internal short ( $R_e = \infty$ ). Then, since  $(E_c^r - E_a) = (E_c^r - E_a^r) = V^r$ , Equation 16 reduces to

$$V = V^r + B \exp \left[ - \frac{2n_c f K_c (t)^{\frac{1}{2}}}{C_c} \right] \quad (18)$$

A comparison of Equation 18 with experiment may be carried out as follows. If  $V^r$ , i.e. the steady state value of  $V$  as  $t \rightarrow \infty$ , is accessible, then\*

$$\ln (V^r - V) = \ln (-B) - \frac{2n_c f K_c (t)^{\frac{1}{2}}}{C_c} \quad (19)$$

That is, for cells with no internal short, a plot of  $\ln (V^r - V)$  versus  $(t)^{\frac{1}{2}}$  will be a straight line at large times (i.e. at times such that  $(V^r - V) \ll RT/F$ ) with a slope of  $-(2n_c f K_c)/C_c$  if mass transfer is rate-controlling.

Since the measurement of  $V^r$  is uncertain due to the very long time required under open circuit stand, an alternative way of comparing Equation 18 with experiment may be proposed as follows. Differentiating Equation 18 with respect to  $(t)^{\frac{1}{2}}$  and taking logarithms, one obtains

$$\ln \left( \frac{dV}{d(t)^{\frac{1}{2}}} \right) = \ln \left( -B \frac{2n_c f K_c}{C_c} \right) - \frac{2n_c f K_c}{C_c} (t)^{\frac{1}{2}} \quad (20)$$

where  $B < 0$ .

Hence, for cells with no internal short and where mass transfer to the electrode is the rate controlling step, a plot of  $\ln (dV/d(t)^{\frac{1}{2}})$  versus  $(t)^{\frac{1}{2}}$  will be a straight line whose slope is identical to that obtained with Equation 19.

### 1.2. When the charge transfer step at the electrode is slow

In such a case, with  $I_{o,c}$  being sufficiently small so that  $1/I_{o,c} \gg (t)^{\frac{1}{2}}/K_c$  in Equation 14, it follows that

$$\frac{d\eta_c}{dt} + \left[ \frac{n_c f I_{o,c}}{C_c} + \frac{1}{C_c(R_e + R_i)} \right] \eta_c + \frac{E_c^r - E_a}{C_c(R_e + R_i)} = 0 \quad (21)$$

Equation 21 is a linear first-order differential equation whose solution is readily obtained as

$$\eta_c = - \frac{E_c^r - E_a}{C_c(R_e + R_i)} \left( \frac{n_c f I_{o,c}}{C_c} + \frac{1}{C_c(R_e + R_i)} \right)^{-1} + B_1 \exp \left[ -t \left( \frac{n_c f I_{o,c}}{C_c} + \frac{1}{C_c(R_e + R_i)} \right) \right] \quad (22)$$

where  $B_1$  is an integration constant.

On substituting for  $\eta_c$  in Equation 7, the final expression is obtained for the dependence of cell voltage on time during the open circuit voltage recovery of a positive-limited nickel-cadmium cell as

$$V = \frac{(E_c^r - E_a)R_c}{(R_e + R_i)} \left[ \frac{n_c f I_{o,c}(R_e + R_i)}{1 + n_c f I_{o,c}(R_e + R_i)} \right] + B_1 \exp \left\{ - \left[ \frac{n_c f I_{o,c}}{C_c} + \frac{1}{C_c(R_e + R_i)} \right] t \right\} \quad (23)$$

\* Since  $V^r$  is always greater than  $V$ ,  $B_1$  must be a negative constant.

Considering the case of a cell which has no internal short ( $R_c = \infty$ ) and since  $(E_c^r - E_a) = (E_c^r - E_a^r) = V^r$ , Equation 23 reduces to

$$V = V^r + B_1 \exp\left(-\frac{n_c f I_{o,c}}{C_c} t\right) \quad (24)$$

A comparison of Equation 24 with experiment may be carried out as follows. Differentiating Equation 24 with respect to  $t$  and taking logarithms, one obtains\*

$$\ln\left(\frac{dV}{dt}\right) = \ln\left(-B_1 \frac{n_c f I_{o,c}}{C_c}\right) - \frac{n_c f I_{o,c}}{C_c} t \quad (25)$$

Hence, for cells with no internal short and wherein charge transfer at the electrode is the rate-controlling step, a plot of  $\ln(dV/dt)$  against  $t$  will be a straight line with a slope of  $(n_c f I_{o,c})/C_c$ .

Depending on which of the two, Equation 20 or Equation 25, is obeyed by experiment, the rate-controlling step may be deduced and the appropriate factor,  $K_c/C_c$  or  $I_{o,c}/C_c$ , from the slope may be used to characterize the possible failure modes of the cell under test.

## 2. Experimental details

The nickel-cadmium cells used were all positive limited, of sintered plate construction and pressure vented; These cells were kindly fabricated and supplied by Vikram Sarabhai Space Centre, Trivandrum, India. Cells designated as P-1 and P-2 each had one positive electrode of 1.75 A h capacity and two negative electrodes of total capacity 2.65 A h (P-1) or 3.69 A h (P-2). Cells P-3, P-4 and P-5 each had two positive electrodes of total capacity 2.85 A h and three negative electrodes of total capacity 5.18 A h (P-3), 4.76 A h (P-4) or 4.10 A h (P-5).

After a reconditioning cycle (charge at  $C/10$  rate for 16 h and discharge at  $C/2$  rate to zero volts) the cell were individually dead-short externally for a given period of time (4, 12 or 16 h), following which the external short was removed and the open circuit voltage recovery transient recorded. The open circuit voltage was measured using an electrometer ( $10^{12} \Omega$  input resistance).

## 3. Results and discussion

The experimental data obtained as outlined above for the spontaneous increase of the open circuit voltage with time of nickel-cadmium cells under near equilibrium conditions are presented in Figs 4 to 6. It may be noted from these figures that for any particular 'dead-short' period prior to the

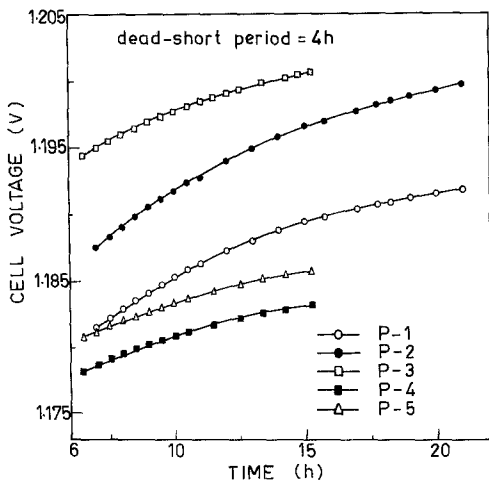


Fig. 4. Open circuit voltage recovery transients of cells P-1 and P-2 (1.75 A h) and P-3, P-4 and P-5 (2.80 A h) after a dead-short period of 4 h.

\* Since  $V^r$  is always greater than  $V$ ,  $B_1$  must be a negative constant.

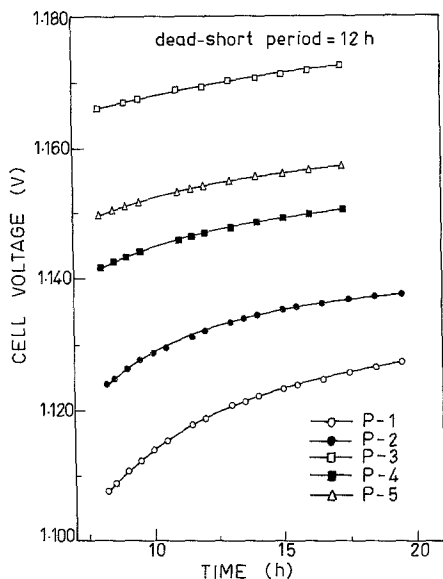


Fig. 5. As for Fig. 4, but with a dead-short period of 12 h.

open circuit study, the voltage recovery rate is faster (or the cell voltage is higher at a given time) for higher capacity cells than for lower capacity cells, except for a dead short period of 4 h where the voltage recovery transients of the cells used could not be resolved based on their ampere-hour capacity. Further, for a given cell, the voltage recovery rate is slower the longer the 'dead-short' period prior to the open circuit study. Finally, the equilibrium value of the open circuit voltage (say, within a drift rate of  $0.1 \text{ mV h}^{-1}$ ) is not attained even after 24 h of open circuit stand. The rate of increase of open circuit voltage in the best case observed (i.e. closest to the steady state) was of the order of  $0.4 \text{ mV h}^{-1}$  for 2.8 A h cells left on open circuit for 32 h, after a 16 h 'dead-short' period (Fig. 3). The highest value of open circuit voltage thus registered is about 1.17 V.

The physical process causing a spontaneous rise in the open circuit voltage of a nickel-cadmium cell has already been identified (see Introduction) as due to diffusion and redistribution of charged (or unreacted) active material from the interior of the pores to the pore surface. The experimental

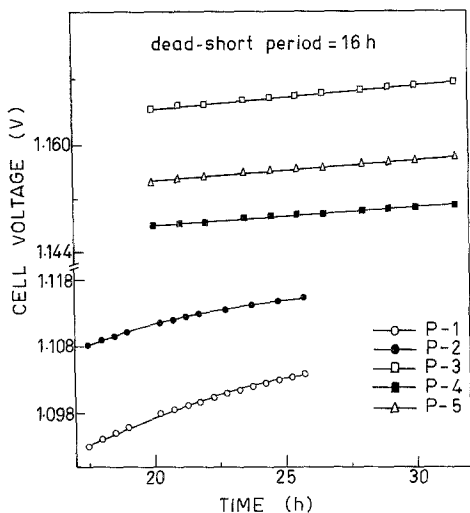


Fig. 6. As for Fig. 4, but with a dead-short period of 16 h.

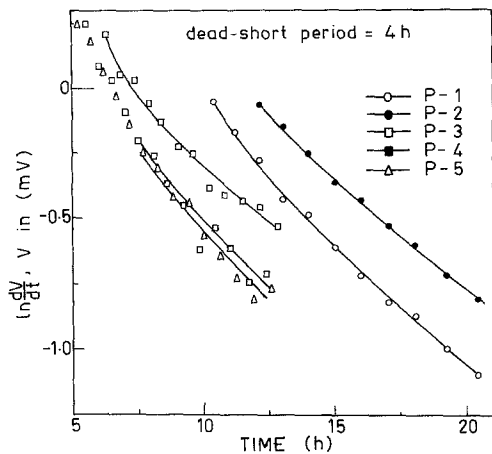


Fig. 7. Dependence of  $\ln dV/dt$  on  $t$  for cells P-1 and P-2 (1.75 A h) and P-3, P-4 and P-5 (2.80 A h) during the open circuit voltage recovery subsequent to a dead-short period of 4 h. (Data derived from Fig. 4).

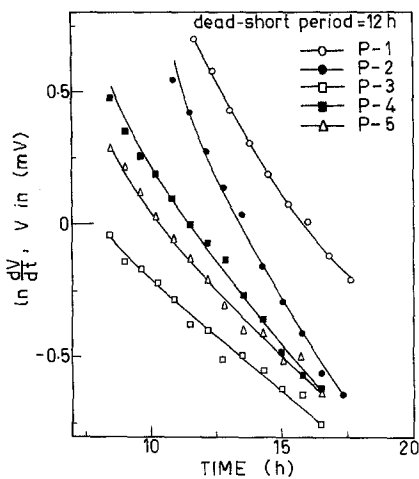


Fig. 8. As for Fig. 7, but with a dead-short period of 12 h. (Data derived from Fig. 5.)

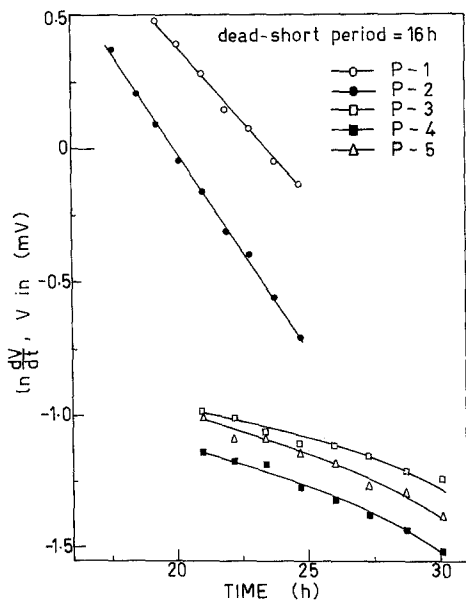


Fig. 9. As for Fig. 7, but with a dead-short period of 16 h. (Data derived from Fig. 6.)



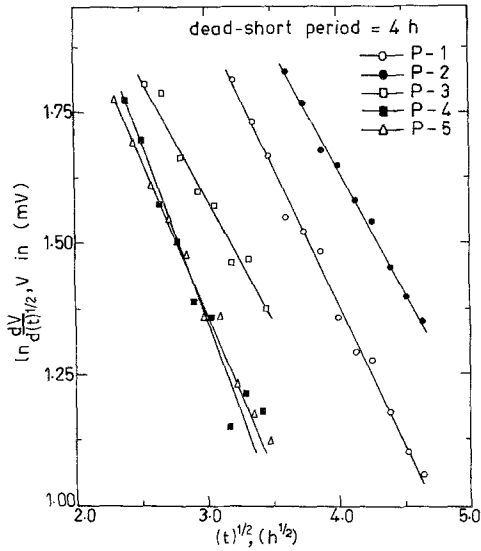


Fig. 10. Dependence of  $\ln dV/d(t)^{1/2}$  on  $(t)^{1/2}$  for cells P-1 and P-2 (1.75 A h) and P-3, P-4 and P-5 (2.80 A h) during open circuit voltage recovery subsequent to a dead-short period of 4 h. (Data derived from Fig. 4.)

data summarized above confirm this model since the true depth of discharge will have an inverse dependence on the cell capacity and a direct dependence on the 'dead-short' period prior to open circuit study.

The quantitative expression for the open circuit voltage recovery transient derived under the theoretical section may now be used to verify the theory by comparison with experiment. For cells without any internal short (as in the present case), the theory predicts that if the open circuit voltage recovery transient is controlled by slow charge transfer then Equation 25 is obeyed, while if it is controlled by slow mass transfer Equation 20 is obeyed.

Plots of  $\ln (dV/dt)$  versus  $t$  derived from the data in Figs 4-6 are presented in Figs 7-9. It may be seen from these figures that, in general, there is a detectable degree of non-linearity in most of the cases, indicating that charge transfer step is not likely to be rate controlling.

Plots of  $\ln (dV/d(t)^{1/2})$  versus  $(t)^{1/2}$  derived from the data in Figs 4-6 are presented in Figs 10-12. It may be seen from these figures that there is a good linearity for practically each case. This confirms the physical model proposed on the basis of slow mass transfer and the theory developed to explain the results quantitatively.

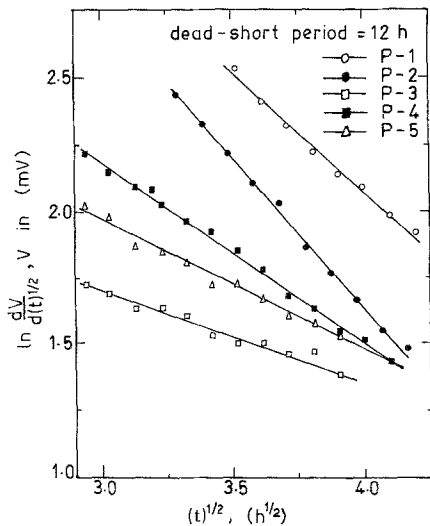


Fig. 11. As for Fig. 10, but with a dead-short period of 12 h. (Data derived from Fig. 5.)

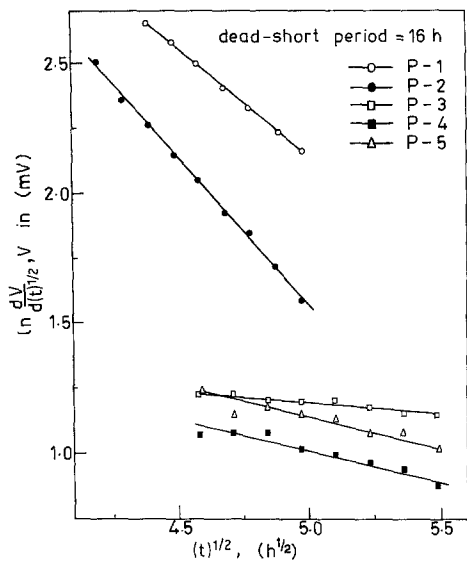


Fig. 12. As for Fig. 10, but with a dead-short period of 16 h. (Data derived from Fig. 6.)

The numerical values of the slopes of the lines in Figs 10–12 are equal to  $-2n_c f K_c / C_c$  from the theory. Since these slopes are obtained by double differentiation of raw data ( $V$  versus  $t$ ), processing errors are unavoidable. Therefore, minor variations in the slopes may not be considered to have any physical significance. However, curves corresponding to the 16-h ‘dead-short’ period prior to the open circuit study (Fig. 12) show a substantial difference between the low capacity cells and the high capacity cells.

The theoretical results are therefore likely to be sensitive to cell characteristics under these conditions of relatively long ‘dead-short’ period. Failure modes which affect the parameters  $K_c$  (for instance, electrode passivation) and  $C_c$  may therefore become predictable, in principle, by monitoring the slope of  $\ln(dV/d(t)^{1/2})$  versus  $(t)^{1/2}$  after a fixed (but sufficiently long) ‘dead-short’ period prior to the open circuit test.

### Acknowledgement

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